

REMARKS/ARGUMENTS

Claims 1, 4-11, and 14-22 are pending.

Claim 19 has been amended.

Claims 2-3 and 12-13 have been cancelled.

Support for the amendments is found in the claims and specification (e.g., page 7, lines 26-34; page 10, lines 13-20; and the Examples), as originally filed.

No new matter is believed to have been added.

The claims are rejected under 35 U.S.C. 103(a) over (a) Costanza et al., US 4,003,871 and (b) Costanza et al. and Gluck et al., US 5,908,872. The rejections are traversed because Costanza et al. alone or in combination with Gluck et al. do not describe or suggest:

(1) adding at least a portion of a dispersant to at least a portion of water containing at least a portion of an oil-soluble free radical initiator (as in step a3 of claim 1);

(2) that a water soluble initiator is active at T_S and an oil-soluble initiator is inactive at T_S ; and

(3) increasing a polymerization temperature from T_S to T_E during which the oil-soluble free radical initiator becomes more active and, therefore, a polymerization efficiency is increased with the increase of the temperature.

(4) In addition, one would not have been motivated to modify emulsion polymerization of Costanza et al. with suspension (bulk) polymerization of Gluck et al. because (i) a polymerization mechanism in suspension is fundamentally different from a polymerization mechanism in emulsion, (ii) Gluck et al. only uses oil-soluble initiators, and (iii) in the Gluck et al. suspension polymerization, feeding of monomers is not conducted (i.e., all monomers are fed at the initial charge).

(5) Costanza et al. teach away from a polymerization at high temperatures and raising the temperature during emulsion polymerization because Costanza et al. explicitly suggest keeping the same temperature during the polymerization and below 80 °C.

The claimed method

The claimed invention is directed to a one step polymerization process of aqueous polymer dispersions producing a low residual monomer content and having a high conversion rate (page 3 of the present specification). The claimed process comprises:

(i) At least a oil-soluble initiator, water and a dispersant are mixed at a starting temperature T_S or lower. Monomers and a water-soluble initiator may or may not be added to the mixture thereafter. However, a dispersant must be added prior to metering monomers as will be explained further.

(ii) The obtained mixture is heated to the temperature T_S (e.g., if the temperature is lower than T_S) and the monomers (the total amount or the remaining amount) are continuously metered into the mixture. The total or main amount of the water-soluble initiator is also added to the mixture.

(iii) The *polymerization is started by the water-soluble initiator at T_S and the temperature is raised from T_S to T_E* and the monomers are continuously fed into the reaction mixture *while* the temperature is increased. The *oil-soluble initiator is inactive at the starting reaction temperature* (i.e., the oil-soluble initiator has a half-life of ≥ 10 hours at the starting reaction temperature T_S) and becomes more active as a temperature approaches the end reaction temperature at which the oil-soluble initiator is fully active (i.e., a half-life of ≤ 5 hours at the end reaction temperature T_E). Polymer particles are formed during this stage of polymerization. The oil-soluble initiator is also a part of the particles (see an explanation below).

(iv) Thus, when the reaction temperature reaches the temperature T_E , the oil-soluble initiator becomes fully active and polymerization of residual unreacted monomer units (within the polymer particles) is carried out by the oil-soluble initiator within the polymeric particles.

As illustrated by the Examples of the present specification, the claimed one-step process produces aqueous polymer dispersions having a low residual monomer content (pages 18-20). For example, the Example on pages 17-18 shows that 5% of the feed I was initially added at 20-25°C and heated to 95 °C. On reaching 95 °C, the remaining amount of the feed I and the total amount of feeds II and III were metered in with constant feed streams during 90 min.

Concerning a dispersant and emulsion polymerization, first, a dispersant, water and an oil-soluble initiator are mixed to solubilize the oil-soluble initiator in water and then monomers and a water soluble initiator can be added. More specifically, adding the dispersant to water creates micelles and also monomer droplets become 'emulsified' by the dispersant. If the dispersant is not used, the oil- soluble initiator would not be homogeneously dissolved into an aqueous phase during the polymerization. The oil-soluble initiator is at least partly dissolved into micelles (i.e., the oil-soluble initiator is enclosed in a micelle like in a cave) and the emulsion polymerization takes place in micelles when monomers are added. During the polymerization, monomer molecules form large droplets of monomers in the aqueous emulsion *migrate through an aqueous phase* into micelles where the polymerization takes place. The oil-soluble initiator and growing polymeric chains are incorporated into micelles to build up polymeric particles during the emulsion polymerization.

Notes: (1) The Examiner is of the opinion that step c_4 is option and, therefore, is given little patentable weight. Applicants respectfully disagree because in c_4 either the total or the remaining amount of monomers is added.

(2) Further, the Examiner has alleged that the amount of the dispersant in step a₃ in claim 17 is “zero” percent in the reaction vessel prior to the monomer metering. Applicants respectfully disagree because claim 17 depends upon claim 1 which requires adding at least one “portion” of at least one dispersion.

“A portion” cannot be “zero” because if it is “zero” then a portion is not added. Thus, although claim 17 limits the amount of the dispersant to “equal or less than 50 wt.%”, the amount of the dispersant in claim 17 cannot be “0” because claim 1 requires adding at least “a portion” of the dispersant and claim 17 comprises all limitations of claim 1 from which it depends and further limits the content of the dispersant to be equal or less than 50 wt.%.

A disclosure of Costanza et al.

Costanza et al. describe a process for preparing high solid content aqueous styrene-butadiene polymer emulsions (col. 1-2). A pre-emulsion is formed comprising water, polymerization monomers, and surfactants (col. 2, lines 10-23, and Example 3). The pre-emulsion is mixed at an ambient temperature prior to the metering into the reactor (10-40 °C, col. 3, lines 46-52). A lypophilic (oil-soluble) and hydrophilic (water-soluble) initiators are added to the pre-emulsion (Example 3). A polymerization reactor is charged with water and a lypophilic (oil-soluble) initiator and is heated to 50 °C (col. 2, lines 28-32; col. 5, line 51 to col. 6, line 56; Example 3, and claim 1). The pre-emulsion is added to the reaction medium in the reactor over, e.g., 2 hours, while the initiation and the polymerization reactions are conducted at the *same temperature* (e.g., at 50 °C) (col. 2, lines 32-35; and Examples 1-4).

Distinguishing the claimed method and the method of Costanza et al.

(1) Costanza et al. describe mixing both a water soluble and an oil-soluble initiators containing no dispersant as the initial charge, while in the claimed method requires introducing at least a portion of a dispersant into the initial charge.

Thus, Costanza et al. do not describe adding at least a portion of a dispersant to at least a portion of water and at least a portion of an oil-soluble free radical initiator (as in step a3 of claim 1) to form micelles with the oil-soluble free radical initiator.

(2) Further, Costanza et al. use a water soluble and an oil-soluble initiators which are both active at the same temperature (e.g., 50 °C as in Example 3), while in the claimed method, the polymerization is started by a water-soluble initiator at T_S , at which the oil-soluble initiator is inactive.

Thus, Costanza et al. do not describe or suggest that a water soluble initiator is active at T_S and an oil-soluble initiator is inactive at T_S .

(3) Also, Costanza et al. describe that the pre-emulsion is metered into a reactor when the reactor is maintained at the same temperature during the initiation and polymerization steps (e.g., 50 °C as in Example 3). Costanza et al. do not describe increasing the temperature during the metering monomers so that the oil-soluble initiator becomes active and conducts a polymerization of residual unreacted monomers inside the polymeric particles.

Thus, although Costanza et al. describe using a mixture of oil-soluble and water-soluble initiators, the polymerization process is conducted at one temperature by both a water- and an oil-soluble initiators, while in the claimed process, the water-soluble initiator starts polymerization at a temperature T_S and the oil-soluble initiator completes polymerization when the polymerization temperature approaches T_E .

(4) Moreover, Costanza et al. do not describe T_E from 80-200 °C as in claim 5.

The Examiner is of the opinion that one would have been motivated to use a high reaction temperature and to increase the temperature in the polymerization process of Costanza et al. as of Gluck et al. Applicants respectfully disagree for the reasons set forth below.

The process Gluck et al. verses the process of Costanza et al.

(a) Gluck et al. describe a batch polymerization in aqueous suspension.

A polymerization mechanism in aqueous suspension is fundamentally different from a polymerization mechanism in emulsion (see above with regard to emulsion polymerization). In aqueous suspension polymerization, small droplets of monomers are formed in water (e.g., by agitation), an oil soluble initiator is added to the aqueous phase so that the oil soluble initiator is dissolved into monomer droplets. All monomer droplets are fed into the initial charge followed by a polymer particle formation in the monomer droplets themselves at the increasing temperature. Thus, polymeric particles have the same size as the monomer droplets. There is no micelle formation and monomer migration through an aqueous phase from large monomer droplets into micelles to build up polymer particles, as in emulsion polymerization.

Thus, the mechanism of the Gluck et al. suspension polymerization is fundamentally different from that of emulsion polymerization of Costanza et al.

(b) Further, the Gluck et al. process comprises using only oil-soluble initiators (e.g., two peroxides that are active at different temperatures) that dissolve into monomer droplets followed by polymerization when the temperature is increased. In the Costanza et al. emulsion polymerization, both benzoyl peroxide (an *oil-soluble* initiator) and potassium persulfate (a *water soluble* initiator) active at the same temperature are used (e.g., see Example 3).

Thus, Gluck et al. and Costanza et al. use a different initiator assistance.

(c) In the Gluck et al. aqueous suspension polymerization, all monomer droplets are fed at the initial charge followed by polymerization at the increasing temperature. A surfactant is added only after 2.5 hours after starting the polymerization (e.g., see Example 1). In the Costanza et al. emulsion polymerization, monomers are fed into the reactor during the polymerization while the temperature is increased from T_S to T_E .

Thus, Gluck et al. and Costanza et al. are fundamentally different with regard to adding monomers, polymerization temperatures and other parameters.

One would not have been motivated to use a high temperature as in the Gluck et al. suspension (bulk) polymerization and also to raise a polymerization temperature during metering of monomers in the Costanza et al. emulsion polymerization with a reasonable expectation of achieving the claimed method or maintaining and/or improving the Costanza et al. emulsion polymerization because:

(i) a mechanism of the Gluck et al. suspension polymerization is fundamentally different from that of emulsion polymerization of Costanza et al. (e.g., the behavior of the components, monomer droplets and polymerization particles; a size and a function of the monomer droplets and polymerization particles; a growing polymeric chain location; temperatures; and initiators, to name a few),

(ii) the Gluck et al. process comprises using only oil-soluble initiators (active at different temperatures), while in the Costanza et al. emulsion polymerization, both an oil-soluble initiator and a water soluble initiators (active at the same temperature) are used, and

(iii) in the Gluck et al. aqueous suspension polymerization, all monomer droplets are fed at the initial charge and monomers are not metered into a reactor while the polymerization temperature is increased.

Further, one would not have reasonably expected that using temperatures adjusted for specific organic peroxides A and B for an aqueous suspension polymerization process would have successfully produced Costanza et al.'s polymer in emulsion which is obtained with different initiators (water and oil soluble), by a different process and a different temperature.

In addition, Costanza et al. teach away from using high temperatures and increasing a temperature during emulsion polymerization because Costanza et al. explicitly suggest keeping the same temperature during the polymerization and below 80 °C.

Thus, Costanza et al. and Gluck et al. do not make the claimed method obvious.

Applicants request that the rejections be withdrawn.

Claims 12, 13, and 19 are rejected under 35 U.S.C. 112, second paragraph. Applicants have amended the claims and it is believe that the claims are clear. Applicants request that the rejections be withdrawn.

A Notice of Allowance for all pending claims is requested.

Respectfully submitted,

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Suspension Polymerization

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Definition: A polymerization process in which the monomer, or mixture of monomers, is dispersed by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. Used primarily for PVC polymerization. Also known as PEARL POLYMERIZATION, BEAD POLYMERIZATION and GRANULAR POLYMERIZATION.

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Related Terms

- [Pearl Polymerization³⁵](#)
- [Bead Polymerization³⁶](#)
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suspension polymerization

chemistry

Main

Aspects of this topic are discussed in the following places at Britannica.

Assorted References

- **Industrial polymerization methods (in chemistry of industrial polymers: Suspension polymerization)**

In suspension polymerization the monomer is dispersed in a liquid (usually water) by vigorous stirring and by the addition of stabilizers such as methyl cellulose. A monomer-soluble initiator is added in order to initiate chain-growth polymerization. Reaction heat is efficiently dispersed by the aqueous medium. The polymer is obtained in the form of granules or beads, which may be dried and...

Citations

MLA Style:

"suspension polymerization." *Encyclopædia Britannica*. 2009. Encyclopædia Britannica Online. 16 Jun. 2009
<<http://www.britannica.com/EBchecked/topic/575625/suspension-polymerization>>.

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Keywords
emulsion, soap

by Dennis Parrish

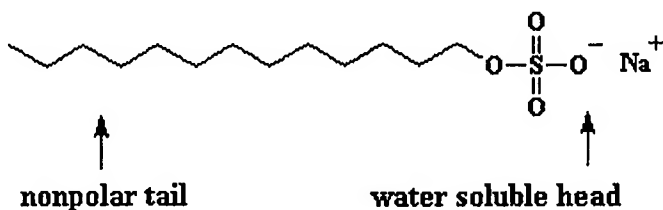
The definition for emulsion is: "A stable colloidal suspension as milk, consisting of an immiscible liquid dispersed and held in another liquid by a substance called an emulsifier".



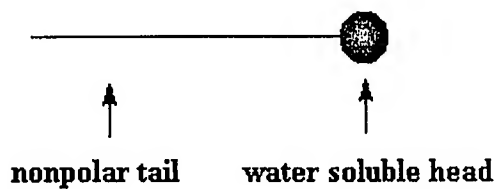
In order to understand emulsion polymerization and emulsifiers, we've got to understand how soap works. Yes, soap! If you already know how soap works and have Grandma's recipe for lye soap, [click here](#) to get to the part on emulsion polymerization. If you're curious, then read on!

Soap's Dirty Job

Soap molecules suffer from a multiple personality disorder, but their dual personalities are always apparent. A soap, or surfactant as it is referred to in emulsion polymerizations, has two ends of different solubility. One end, termed the tail, is a long hydrocarbon that is soluble in nonpolar, organic compounds. The other, the head, is often a sodium or potassium salt, which is water soluble. The water soluble salt can be the salt of a carboxylic acid or sulfonic acid. The technical term for the chemical display of "dual personalities" is *amphipathic*.

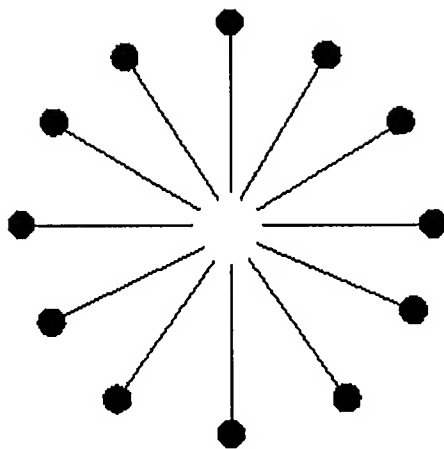


Sodium Lauryl Sulfate



Lazy chemist's representation of
Sodium Lauryl Sulfate

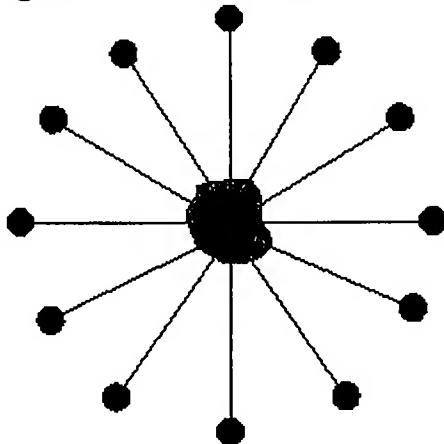
One soap molecule isn't much good to you. But when you get a whole bunch of 'em together, neat stuff starts to happen. At a certain concentration in water, soap molecules congregate and form micelles. Scientists have an apt (if not original) name for this called the critical micelle concentration, or CMC for short. Don't let the scientists fool you; they're really doin' the hokey pokey, tails inward.



Any dirt, grease, or grime that you happen to have on your hands is most likely organic and looks like this:



When you wash your hands with soapy water the hokey pokey party really gets goin'. The jubilant dirt particle jumps right in the middle where it's pretty happy. It doesn't want to get out so it stays dissolved in the organic tails of the micelle.



Now the dirt is dissolved in the micelle, and the micelle is dissolved in water, and...Voila! With copious amounts of water, you can wash everything down the drain.

Party Pooper.

Now a question for you: Why is it difficult to take a bath in the ocean?

Finally...Emulsion Polymerization

In an emulsion polymerization, the soap, or surfactant, is dissolved in water until the critical micelle concentration (CMC) is reached. The interior of the micelle provides the site necessary for polymerization. A monomer (like styrene or methyl methacrylate) and a water soluble free radical initiator are added and the whole batch is shaken or stirred (sorry, James Bond). Emulsion polymerizations are always performed free radically. Anionic and cationic chain ends would be rapidly quenched by the water. The product of an emulsion polymerization is called a latex; does the term "latex paint" ring a bell?

Location, Location, Location

Once everything is thrown in the pot, the monomer can be found in three different places. First, it can be in large monomer droplets floating around aimlessly in the water. Second, some of the monomer may be dissolved in the water, but this is unlikely. Remember, organic monomers like styrene and methyl methacrylate are hydrophobic. Lastly, the monomer may be found in micelles, which is exactly where we want it. Now look back at the definition at the beginning of this page. The immiscible liquid is the hydrophobic monomer, the mother liquor is water, and the emulsifier is soap.

Initiation and Polymerization

Initiation takes place when an initiator fragment migrates into a micelle and reacts with a monomer molecule. Water soluble initiators, such as peroxides and persulfates, are commonly used (This also prevents polymerization in the big monomer droplets). Once polymerization starts, the micelle is referred to as a particle. Polymer particles can grow to extremely high molecular weights, especially if the initiator concentration is low. That makes the radical concentration and the rate of termination low as well. Sometimes a chain transfer agent is added to the mix to keep the molecular weight from getting too high.

Propagation

Monomer migrates from the large monomer droplets to the micelles to sustain polymerization. On average, there is one radical per micelle. Because of this, there isn't much competition for monomer between the growing chains in the particles, so they grow to nearly identical molecular weights and the polydispersity is very close to one. Practically all the monomer is consumed in emulsion polymerizations, meaning the latex can be used without purification. This is important for paints and coatings. Just add some color to the latex, pour it into a can, and it's ready to use.

Here's the neat aspect of emulsion polymerization: each micelle can be considered as a mini bulk polymerization. Unlike traditional bulk polymerizations there is no unreacted monomer leftover, and no thermal "hot spots" form. In bulk polymerizations (no solvent, just monomer and initiator), thermal hot spots cause degradation and discoloration and chain transfer broadens the molecular weight distribution. An increase in temperature sometimes cause the rate of polymerization to increase explosively. The water here acts as a heat sink for all those mini reactors and keeps them from blowing up! Pyromaniacs don't do emulsion polymerizations.

Molecular Weight

Now this is cool too: The rate of polymerization is the same as the rate of disappearance of monomer. Monomer disappears faster when there are more particles. In order to have more particles there must be more micelles. If the soap sud concentration is increased, this ought to give us more micelles. Now suppose the concentration of initiator is left the same. This will give us more particles and less radicals. What this means is the number of radicals per micelle drops below one. In other words, the rate of termination will be low since there are less radicals. WHEW!

So the end result is this: *decreasing the initiator concentration increases molecular weight and rate of polymerization!* This is completely opposite from bulk and solution polymerization. To increase the rate of polymerization for those you have to heat the reaction or increase the initiator concentration, both of which increase the rate of termination and lower the molecular weight.

Practically Speaking

Sounds neat, but is it useful? Sure is. Poly(vinyl acetate), polychloroprene, polymethacrylates, poly(vinyl chloride), polyacrylamide, and copolymers of polystyrene, polybutadiene, and polyacrylonitrile are made commercially by emulsion polymerization.

Congratulations!

You've waded through the muck to get this far, unless, of course, you skipped down to the bottom to see if anything cool was here. The set-up now gets paid off with this handy-dandy, easy to decipher table that lists the good and the bad (and, believe me, it's all ugly!).

Polymerization Process	The Good	The Bad
Bulk	Only monomer is present--no extra stuff, High molecular weights	Thermal hotspots, High viscosity, Unreacted monomer present
Solution	Easy temperature control, Control of molecular weight	Must remove solvent, Chain transfer to solvent
Emulsion	All monomer reacts, Latex is usable "as is", Thermally controllable, Can make low Tg materials, Low viscosity	Presence of surfactant may cause water sensitivity

References and Further Reading

(i.e., more complicated and detailed reading)

Odian, G., "Principles of Polymerization" 3rd Ed., John Wiley and Sons, Inc., New York, 1991.

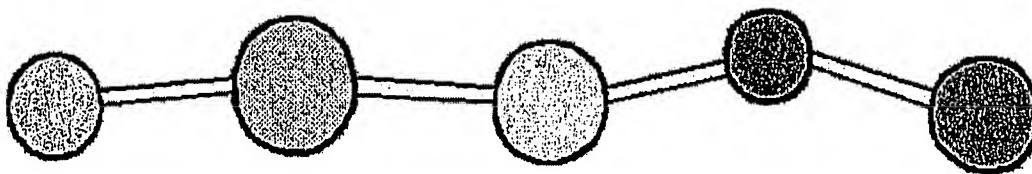
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